Electronic Structure of Boron Oxides Measured by Soft X-Ray Emission Spectroscopy

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INTRODUCTION

Boron oxides (B_2O_3) are important materials especially in the ceramic and glass industries, and are also interesting materials from the viewpoint of materials science. Generally, they have rather complex crystal structures, which result in a variety of optical characteristics. Therefore, it is important to understand the fundamental chemical bonding structure in B_2O_3. The characterization of B_2O_3 and borate glasses has been investigated mainly by optical spectroscopy [1], and many theoretical studies [2, 3] have been intensively conducted. However, there has been little study of characterization using soft x-ray spectroscopy. Soft x-ray spectroscopy using monochromatized highly brilliant synchrotron radiation has become a powerful tool for electronic structure analysis [4]. We therefore measured the soft x-ray emission/absorption spectra and photoelectron spectra of B_2O_3 to elucidate the electronic structure and band structure. In this paper, high-resolution soft x-ray emission spectra in the B *K* and O *K* regions and photoelectron spectra are described to reveal the valence structure. Selectively-excited B *K* and O *K* x-ray emission spectra are also described to study the band structure.

EXPERIMENT

Commercially obtained bulk B_2O_3 samples were used for spectral measurements of soft x-ray emission and absorption. Soft x-ray emission measurements of B_2O_3 were performed using a grating x-ray spectrometer at BL-8.0. The excitation energy of the incident beam was varied from the threshold to the continuum in both the B *K* and O *K* regions to elucidate the radiative decay process of the inner-shell excitation. X-ray absorption measurements were performed at BL-8.0 using a fluorescence yield (FY) method and at BL-6.3.2 using a total electron yield (TEY) method. Photoelectron spectra of B_2O_3 thin films were measured at the Photon Factory [5].

RESULTS AND DISCUSSION

(1) Valence Band Structure: Figure 1 shows the soft x-ray emission spectra of bulk B_2O_3 in the B *K* and O *K* regions, and the photoelectron spectrum of the B_2O_3 thin film. These spectra were taken in the “off-resonance” excitation. The excitation energy in the x-ray emission measurements was tuned to about 20 eV higher than the threshold (209.6 eV for B *K* and 550 eV for O *K*) and that in the photoelectron measurements was tuned to about 20 eV lower than the B *K* threshold (175.6 eV). In the figure the energy scale of these spectra is normalized and aligned from the Fermi edge. The density of states (DOS) spectra of B_2O_3 calculated by Li et al. [2] using a first-principles calculation with a local-density approximation (LDA) were superimposed on the soft x-ray emission spectra: the s- and p-portions of the boron DOS were superimposed on the B *K* spectrum and those of the oxygen DOS on the O *K* .

In the B *K* x-ray emission spectrum, a main peak was observed at 181 eV with a high-energy tail and low-energy satellite at 167 eV. In the O *K* x-ray emission spectrum, a sharp main peak was observed at 525.5 eV with a small peak at 520 eV. These measured spectral features of the B *K* and O *K* x-ray emission are approximately in agreement with the p-portion in the calculated

DOS spectra. Therefore, the main peak with the high-energy tail in the B *K* XES can be assigned to B2p, and the low-energy satellite to hybridized B2p-O2s. The two-peaked structure of the O *K* XES can be assigned to O2p. In the photoelectron spectrum, three peaks were observed at the binding energy of -8 eV (denoted as E_1 in the figure), -12 eV (E_2), and -26 eV (E_3). The spectral feature of this photoelectron can be assigned by comparing the B *K* and O *K* x-ray emission spectra as follows: E_1 is due to O2p, E_2 is mainly B2p and slightly O2p, and E_3 is B2p, B2s, and O2s. The tail near -15 eV is mainly B2s.

(2) Radiative Decay Process: Figure 2 shows the excitation-energy-dependence of the B *K* x-ray emission spectra. The excitation energy was varied from 191.6 eV below the threshold to 224.6 eV on the continuum. In the 224.6-eV excitation, we observed a main peak at 181 eV assigned to B2p, a low-energy satellite at 167 eV assigned to B2p-O2s, a high-energy satellite at 194 eV, and a small peak at 175 eV. The 175-eV peak can be assigned to the third-order diffraction of the O *K* x-ray emission peak, because this peak energy corresponds to one-third of the peak energy of O *K* x-ray emission, and the peak shape is independent of the excitation energy from the B *K* threshold to the continuum. Both the main peak and low-energy satellite shifted about 2 eV toward lower energy during the π*-excitation at 193.6 eV. This peak shifting can be explained by the change in initial- and final-state screening effects produced by the absence of the electron excited to the bound excitonic π* orbital [4], which is the “spectator” resonant inelastic x-ray scattering (RIXS). The intense emission peak near 194 eV in the 193.6-eV excitation is the “participator” resonant elastic x-ray scattering (REXS) due to the π*-B1s transition of the participator electrons [6]. The positions of the main peak and the low-energy satellite were almost independent of the excitation energy above 193.6 eV of the π* state. This suggests that the band structure of B_2O_3 is fairly non-dispersive in the B2p valence and conduction band, which is consistent with the theoretically calculated band structure [2].

Figure 3 shows the excitation-energy-dependence of O *K* x-ray emission spectra and the FY-absorption spectrum. The excitation energy was varied from 532 eV below the threshold to the continuum at 560 eV. In the absorption spectrum, a prominent peak observed at 536.5 eV may be assigned to the π* state. In the x-ray emission spectra, the main peak assigned to O2p slightly shifted depending on the excitation energy. This slight peak shifting at the π*-excitation is due to the spectator RIXS. However, no REXS via π*-state was observed in the O *K* region. These slight shifts of the main peak and the absence of REXS show that the bound electron state of the π*-orbital in O *K* threshold is weaker than that in B *K*. The lack of any shifting of the main peak in the higher-energy excitation above π*-state also shows that the band structure is non-dispersive, which is consistent with theoretical band calculations [2].

CONCLUSION

Soft x-ray emission spectra in the B *K* and O *K* regions of B_2O_3 were measured, and the valence band structure of B_2O_3 was revealed from the hybridized B-O bondings by comparing these spectra with the photoelectron spectrum of B_2O_3 thin films and theoretical DOS spectra. Although resonant radiative decay processes such as “spectator” RIXS and “participator” REXS were strongly observed at the π*-excitation in the B *K* threshold, weak resonant radiative decay phenomena were observed in the O *K* threshold. This shows that the bound electron state at the π* orbital in boron atoms is stronger than that in oxygen atoms. No significant peak shifts were observed in the selectively-excited x-ray emission spectra in the B *K* and O *K* thresholds, which shows that the band structure is fairly non-dispersive. These spectral features are in agreement with the theoretically calculated band structure.

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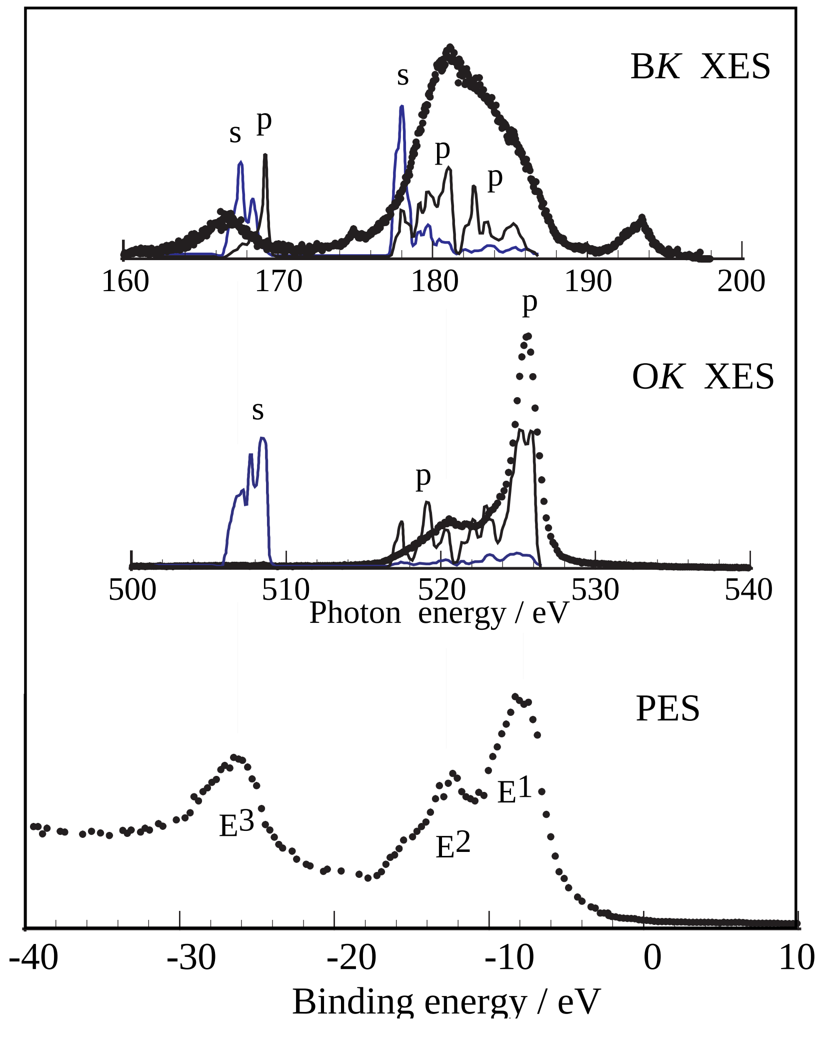

Figure 1 The upper two spectra show the B *K* and O *K* x-ray emission of bulk B_2O_3, and the lower one shows the photoelectron spectrum of B_2O_3 thin film (dotted lines). All spectra were off-resonance spectra: the excitation energies were 209.6 eV for B *K* x-ray emission, 550 eV for O *K* x-ray emission, and 175.6 eV for the photoelectron spectrum. Theoretical DOS spectra (solid lines) of valence orbitals in boron and oxygen atoms, calculated by Li et al. [2], are superimposed on individual B *K* and O *K* x-ray emission spectra.

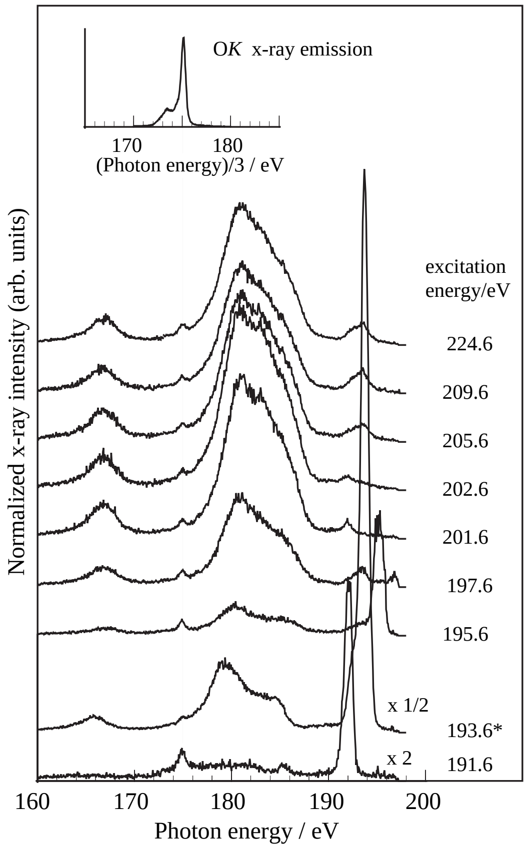

Figure 2 B K x-ray emission spectra of bulk B_2O_3 in which the excitation energy was varied from 191.6 eV to 224.6 eV. The O K x-ray emission spectrum, in which the horizontal axis shows the third-order diffraction energy, is superimposed.

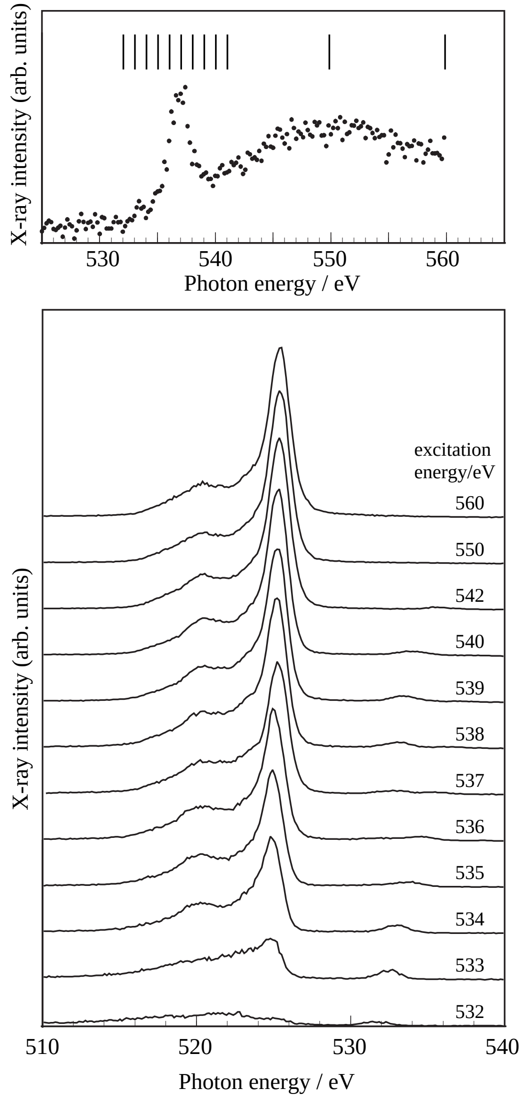

Figure 3 The upper panel shows the FY x-ray absorption spectrum of bulk B_2O_3. The excitation energy positions are marked with bars. The lower panel shows the O K x-ray emission spectra of bulk B_2O_3, in which the excitation energy was varied from 532 eV to 560 eV.

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